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Silanol-rich Platelet Silica Modified with Branched Amine for Efficient CO$_2$ Capture

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Abstract

In this work, we report a new route to improve the CO$_2$ adsorption performance of solid amine adsorbents. Platelet mesoporous silicas with abundant surface silanols were prepared by emulsion synthesis followed by simple solvent extraction. These silanol-rich silica particles were then functionalized with branched polyethyleneimine (BPEI) by grafting or impregnation to prepare CO$_2$ adsorbents. Silanol-rich silicas grafted with BPEI exhibited 70% higher amine density and 47% higher CO$_2$ adsorption capacity than its calcined counterpart. The adsorbent achieved a maximum CO$_2$ adsorption efficiency up to 13.82 mmol CO$_2$/ g-BPEI. Adsorbed species found in the infrared spectra suggested that silanols may contribute to the enhanced CO$_2$ adsorption efficiency on grafted amines. Silanol-rich silica functionalized with BPEI retained more porosity than its calcined counterparts, which may account for its superior CO$_2$ adsorption capacity. Silanol-rich silica impregnated with amines achieved the highest CO$_2$ adsorption efficiency ever reported (5.65 mmol/ g, 526.7 mg/ g-BPEI). Adsorption kinetic modeling confirmed that silanol-rich adsorbent provides better CO$_2$ diffusion pathways. These potential benefits of silanol-amine interaction, coupled with platelet mesoporous structure and branched polyamine chains, opens a new pathway to high-performance adsorbents for CO$_2$ capture.

Keywords: pore structure; silanol-amine interaction; CO$_2$ adsorption kinetics
1. Introduction

Industrial combustion of fossil fuels has raised significant concern over greenhouse gas emissions, predominantly carbon dioxide (CO$_2$). The state-of-the-art carbon capture and sequestration (CCS) offers a promising solution to CO$_2$ mitigation. However, the well-established CCS technology of liquid amine absorption has several inherent drawbacks such as low amine efficiency, equipment corrosion and large energy consumption for recycling. Solid adsorbents, such as zeolites, metal oxides, metal-organic frameworks (MOF), and solid amine adsorbents have therefore emerged as promising alternatives for CO$_2$ capture. Among these adsorbents, amine-functionalized mesoporous silica has received intensive research attention due to its tunable pore structures and high adsorption capacity under industrial relevant conditions.

Organic amines can be attached to the silica surface via chemical grafting or physical impregnation. To date, most studies on porous silica-amine adsorbents adopt linear short chain amines, such as diethylenetriamine (DETA), tetraethylenepentamine (TEPA) and polyethyleneimine (PEI, M$_w$ < 800). Despite their high amine content and good accessibility to CO$_2$, short chain amines suffer from serious leaching and degradation. Long chain polyethyleneimine (PEI, M$_w$ > 10000) has emerged as a potential alternative because of its superior stability. However, diffusion barrier into highly viscous amine films has limited their CO$_2$
capture performance at industrial temperature (45-75 °C). In contrast, branched amines with medium molecular weight possess lower viscosity and higher thermal stability. It is thus important to optimize the adsorption performance by choosing adequate amines or tailoring the pore structure. Pore structure can be tuned by shortening the pore channel\textsuperscript{13,14} or enlarging the mesopores\textsuperscript{15,16}.

Foreign species such as hydroxyl groups also play a role in CO\textsubscript{2} adsorption. Wang et al. reported that hydroxyl-containing surfactants increased the mobility of CO\textsubscript{2} inside the pores\textsuperscript{17}. Rich hydroxyl groups in poly (ethylene glycol) also increased the amount of adsorbed CO\textsubscript{2} per amine molecule by cooperative adsorption\textsuperscript{18-20}. Considering the similar chemical nature of silanols (Si-OH) and hydroxyl groups (C-OH), we hypothesize that surface silanols may as well improve amine dispersion and CO\textsubscript{2} adsorption. Unlike hydroxyl-containing organics which occupy the pores, surface silanols does not affect the pore volume, thereby preserving a porous structure for amine loading and CO\textsubscript{2} diffusion.

Surface silanol density can be tuned by different template removal methods, namely calcination and extraction. In this study, the surface silanol density of platelet silica was tuned by calcination or extraction. Then the mesoporous platelet silica was functionalized with branched polyethyleneimine (BPEI) via grafting or impregnation. Extraction preserves more reactive surface silanols, which contributes to the amine functionalization and CO\textsubscript{2} adsorption process. CO\textsubscript{2} dynamic capture tests were carried
out to investigate the effects of (i) porous structure; (ii) amine type; (iii) amine loading; (iv) adsorption temperature. The main goal was to illustrate the effect of surface silanols in a highly efficient CO$_2$ adsorbent.

2. Experimental

2.1 Reagents

Pluronic P123 [(EO)$_{20}$(PO)$_{70}$(EO)$_{20}$; EO = $\text{CH}_2\text{CH}_2\text{O}$–, PO = $\text{CH}_2(\text{CH}_3)\text{CHO}$–] was purchased from Aldrich. Tetraethyl orthosilicate (TEOS, > 99 %), $\gamma$-Chloropropyltriethoxysilane (Cl-PTES), branched polyethyleneimine (BPEI, 99 %, M.W. = 600/1800/10000, 99 %, density 1.0300 g·cm$^{-3}$) were purchased from Aladdin Chemistry Co., Ltd, China. All reagents were used without further purification. 1.6 M HCl solution was prepared from saturated HCl (37 %).

2.2 Synthesis of the silica supports

Mesoporous platelet silica was synthesized following the method of Zhang et al.$^{13}$. In a typical procedure, 4.0 g of Pluronic P123 was dissolved in 140 mL HCl solution (1.60 M), and then 0.041 g of NH$_4$F was added as an etching agent to expand the pores. The mixture was continuously stirred at 40 °C until the solution became clear. 23.00 g decane and 8.50 g TEOS were premixed and then introduced into the solution under mechanical stirring (400 rpm) (final P123/HCl/NH$_4$F/H$_2$O/TEOS/decane molar ratios were 1/261/1.8/11278/x/y; x = 48-77, y = 0-755). The above mixture was stirred at 35 °C for 20 h, and then transferred into an autoclave for hydrothermal
reaction at 100 °C for 48 h. The products were collected by filtration, dried in air. The template was removed by:

1) Calcination. Dried silica was placed in a quartz tube and heated at 550 °C for 6 h under an air flow. The calcined product was designated as SC-x-y.

2) Extraction. 1 g of dried silica was mixed with 50 mL of ethanol (99.5 %) and 1 mL H₂SO₄. The mixture was refluxed at 78 °C for 12 h. The extracted product was designated as SE-x-y.

Two other calcined supports were also prepared and functionalized with amines. Conventional SBA-15 was synthesized following Zhao et al. Calcined short pore fluorosilica (SCF) was prepared with NH₄F but without decane. The platelet silicas with molar ratio of 1: 60: 235 were extensively investigated. They are abbreviated as SC and SE in the following, referring to silica calcined and extracted adsorbents, respectively.

2.3 Preparation of amine functionalized solid adsorbent

Amine modified silicas were prepared by wet impregnation and chemical grafting. For grafting, BPEI was tethered onto the support via silanol condensation and the followed substitution of the chlorine atom. Specifically, 2.0 g SC was dehydrated in vacuum at 80 °C for 1 h, and then dispersed in 100 mL dried toluene. 2.0 mL Cl-PTES was added, and further kept under reflux for 12 h. The product was filtrated, washed out with toluene, and dried in vacuum at 70 °C. The product was denoted as
SC-G, referring to the chlorine group on it. Subsequently, 1.0 g SC-G was dispersed in 50 mL ethanol, and 2 g BPEI was added to the suspension. The suspension was refluxed for 12 h, filtrated, washed with ethanol and vacuum dried at 80°C. The grafted product was denoted as SC-G-BPEI. BPEI was grafted onto SE following the same procedures. The Cl-PTES modified SE and the prepared adsorbent were denoted as SE-G and SE-G-BPEI, respectively.

For wet impregnation, the desired amount of BPEI of different molecular weight (600, 1800 and 10000) was completely dissolved in ethanol with stirring at 60 °C and cooled down to 30 °C. The silica support (from 0.4 to 0.9 g) was added into the mixture (Table 1), stirred for 3 h and transferred into a petri dish and placed in fume hood for 1 h evaporation. The obtained solid was further dried under vacuum at 80 °C overnight. The resulting adsorbents were denoted as SE-I-BPEI-w, where w denotes the weight percentage of BPEI in the adsorbent.

2.4 Physical and chemical characterization

Scanning electron microscope (SEM, S4800, Hitachi, Japan) and transmission electron microscope (TEM, JEM-2010HR, JEOL, Japan) was used to observe the morphology and microstructure of the samples.

The nitrogen adsorption-desorption characterization on the samples was performed at 77.35 K with an automatic gas adsorption instrument (ASAP 2020, Micromeritics Corp., USA) at the range of relative pressure from $10^{-6}$ to 1. The surface area was
calculated by Brunauer-Emmett-Teller method (BET) and pore size distribution was calculated by Kruk-Jaroniec-Sayari relation (KJS) from the adsorption branch. Thermogravimetric analysis (TGA) was performed on Netzsch TG-209. The samples were preheated to 100 °C and kept in a nitrogen flow (30 mL/min) for 10 min, and heated to 800 °C at a heating rate of 10 °C/min. Silanol mass was measured from the mass loss between 200 and 800 °C.

FTIR spectra in the range of 650 to 4000 cm\(^{-1}\) were measured on a Bruker Tensor 27 instrument. For sample preparation, the amine silica adsorbents were mixed with KBr, pressed to be self-supporting pellets and treated at 150 °C in dynamic vacuum conditions (~10\(^{-6}\) Torr) for 6 h. Afterwards, they were transferred to the IR cell for measurement in air. For the CO\(_2\) sorption samples, the pellets were exposed to a dry 10 % CO\(_2\)/N\(_2\) flow at 30 °C for 30 min after vacuum treatment and immediately transferred onto the IR cell which was completely sealed throughout the measurement to avoid further adsorption of water and CO\(_2\). The results were analyzed with OMNIC 8 software (Thermo Scientific).

\(^{29}\text{Si}\) solid-state nuclear magnetic resonance (\(^{29}\text{Si}\) NMR) was performed on an AVANCE AV spectrometer (Bruker Co., Ltd., Swiss) operating at 400MHz and with a 4 mm CP/MAS broadband probe. Chemical shifts are quoted relative to tetramethylsilane. Intensity information was obtained by spectral deconvolution.
Elemental analysis was carried out on Elementar Vario EL (Elementar Analysen systeme GmbH, Germany)

\[\text{C1s X-ray photoelectron spectroscopy (XPS) was carried out on ESCALAB 250 (Thermo-VG Scientific) equipped with a 500 mm Rowland circle with an Al anode coupled with Mg K}\alpha \text{ radiation (1253.6 eV). Each powder sample was pressed onto a piece of double-sided sticking tape and mounted on the sample probe. After degassing at } \sim 10^{-5} \text{ Torr, the sample was transferred to the analyzer chamber (<7 } \times 10^{-9} \text{ Torr).}

2.5 Adsorption characteristics

In a typical adsorption-desorption process, 0.5 g of the adsorbent were dried in a vacuum at 120 °C. The adsorbent was then placed into a home-built adsorption column (Φ = 1.3 cm). A dry nitrogen flow was introduced into the column at a flow rate of 30 mL/min for 0.5 h to remove all residual water, and then switched to dry simulated flue gas (30 mL/min, 10 % CO\textsubscript{2} and 90 % N\textsubscript{2}). The inlet and outlet concentrations of CO\textsubscript{2} were determined by an Agilent 6820 gas chromatography equipped with a thermal conductivity detector. The adsorption amount was calculated as follows:

\[Q = \int_{0}^{t} \left( C_{in} - C_{eff} \right) \cdot V \cdot dt \div 22.4 \cdot W\]

Where Q is the dynamic CO\textsubscript{2} adsorption capacity of the (mmol CO\textsubscript{2}/g); t is the adsorption time (min); \(C_{in}\) and \(C_{eff}\) are the influent and effluent flow rate of CO\textsubscript{2}
(mL/min), respectively. V is the total flow rate (30 mL/min); W is the weight of absorbent (g) and 22.4 is the gas molar volume (mmol/mL). After adsorption, the adsorbents were regenerated by N$_2$ flow at 80 °C for 30 min.

3. Results and discussions

3.1 Pore structure of platelet silica

Based on previous reports on the advantages of platelet morphology$^{14, 15}$, the platelet particles were selected from series of mesoporous silica synthesized at different reactant ratios (Figure S1). The remaining templates were removed by calcination or extraction. Particle morphologies and pore structure were characterized by TEM observation as well as N$_2$ adsorption-desorption. The prepared silicas were uniform platelet particles with ordered hexagonal pore structure (Figure 1).

For platelet silica, it is estimated from the TEM graph that pore length L = 300 nm and radius R = 200 nm, thus diameter D = 2·R = 400 nm. The corresponding aspect ratio (AR) is given by: AR = L/ D = 0.75. The AR of platelet silica is much lower than that of conventional SBA-15 ($\sim$ 2.5)$^3$, indicating that platelet silica provides better pore diffusion pathways$^{13}$. The most probable pore size of SC and SE was 13.5 nm and 13.8 nm, almost twice the size of conventional SBA-15 (7.4 nm). Larger pore size also plays a role in improving amine accessibility and CO$_2$ diffusion.

N$_2$ adsorption and desorption isotherms provided key information about surface and porosity (Figure 1b, Table 2). Steep adsorption of N$_2$ at very low relative pressures
can be attributed to the micropores formed by the PEO segment of the surfactant during synthesis\(^4\), or monolayer-multilayer surface adsorption of \(\text{N}_2\) on the materials\(^{24}\). The adsorption branch of both isotherms showed clear adsorption hysteresis of a Type IV isotherm at relative pressure of \(~0.7\) to \(~0.75\), due to capillary condensation into large mesopores\(^4,5\). The increase in \(\text{N}_2\) adsorption at \(p/p_0 > 0.98\) is related to slit-shaped macropores larger than 50 nm (Figure 1a).

To characterize the difference in surface silanol density, thermogravimetric measurements were carried out on both silica supports (Figure 2). According to Peng et al.\(^{19}\), the three-step mass losses in TG graph of silica materials are 1) 100 °C to 200 °C - physically adsorbed water on surface; 2) 200 °C to 800 °C - surface silanols. 3) 800 °C to 1000 °C - internal silanols. Therefore, the mass of surface silanols can be attained from the mass loss from 200 to 800 °C. Along with the surface area data, we can estimate the silanol density on the silica surface. Wang et al.\(^{20}\) also adopted this method to calculate silanol densities on the silica surface. For SC, silanol condensation accounted for the total weight loss of 5.64 % above 200 °C. The corresponding silanol density was 6.27 mmol/ g. Pure P123 (Aldrich, \(M_w = 5800\)) completely decomposes between 250 °C and 380 °C. For SE, the continual weight loss of 9.79 % over 380 °C could be all assigned to dehydroxylation of silanols\(^{20}\). The surface silanol density is calculated based on the following stoichiometry:

\[2\text{Si} - \text{OH} \xrightarrow{\Delta} \text{Si} - \text{O} - \text{Si} + \text{H}_2\text{O}\]
\[ n_{Si-OH} = 2 \cdot m \cdot M_{H_2O} \]

Where \( n_{Si-OH} \) (mol) is the molar quantity of silanols, \( m \) (g) is the mass loss in the curve from 200 to 800 °C, and \( M_{H_2O} \) (18 g/mol) is the molar mass of water.

The estimated silanol density of SE was at least 11.0 mmol/g, 75.0% higher than that of SC. Based on the BET surface area \( S_{BET} \) of both supports, the surface silanol density \( D_{Si-OH} \) (nm\(^{-1}\)) can be calculated as:

\[ D_{Si-OH} = \frac{n_{Si-OH}}{S_{BET}} \cdot N_A \]

where \( N_A \) is the Avogadro constant (mol\(^{-1}\)). Therefore, the estimated silanol surface coverage is 6.65 Si-OH/ nm\(^2\) for SC and 11.0 Si-OH/ nm\(^2\) for SE.

### 3.2 Effect of silanols on amine functionalization onto platelet silicas

To understand the effect of amine functionalization and silanol density on pore structures, \( N_2 \) adsorption-desorption isotherms of BPEI functionalized silica are compared (Table 2, Figure 3). A narrower hysteresis in SE-G-BPEI indicated a more uniform pore structure after amine grafting. SE-G-BPEI also adsorbed more \( N_2 \) at \( P/P_0 > 0.95 \), indicating that more macropores are present. Despite the 70 % higher amine loading, SE-G-BPEI retained a comparable surface area and 15 % higher pore volume than in SC-G-BPEI (Table 2). These results confirmed the higher porosity in SE-G-BPEI adsorbents after amine grafting. SC-I-BPEI-10 (Figure 3) adsorbed less \( N_2 \) than the silica support SC (Figure 1) at \( P/P_0 < 0.01 \), indicating that micropores are blocked by BPEI, which may explain the decrease in surface area after 10 % amine loading. Interestingly, the surface area and pore volume of SE-I-BPEI-50 were 4.9
and 2.8 times higher than SC-I-BPEI-50 (Table 2). Since SC and SE had comparable pore parameters, the silanol density should be the main reason for higher porosity in SE-I-BPEI-50.

The impregnation process can be explained by two competing forces: amine-silanol ionic interaction against amine-solvent hydrogen bonds. In the BPEI-ethanol solution, surface silanols form ionic pairs Si-O⁻N⁺HR₂ with amine groups. Calcined silica has a limited amount of surface silanols, thus weak ionic interactions. Upon solvent evaporation, the escaping solvent molecules attracted the amine chains, which dispersed around pore mouth and caused pore blockage. For example, SC-I-BPEI-10 lost 48% of pore volume with only 10% amine loading. In contrast, extracted silica has more surface silanols inside the pores, and thus stronger interactions with BPEI chains, forming a “cylindrical layer” that is more stable upon solvent evaporation. As a result, the extracted adsorbent SE-BPEI-50 preserved a higher porosity than its SC counterparts. To better illustrate the abovementioned effect of surface silanols, we propose a “cylindrical surface coating” mechanism. (Scheme 1).

Thermogravimetric analysis (TGA) elucidated the surface interactions and amine distribution of amine-impregnated silica adsorbents (Figure 4). The TGA curves for SC adsorbents are very similar to those for the SE adsorbents. For clarity, we only show the curves for SE-I-BPEI. The first stage from 100 to 200 °C is attributed to pre-adsorbed species, mainly physisorbed water and CO₂. The amount of pre-adsorbed
species increased with amine loading due to the hydrophilic silanols and basic amine groups of BPEI. This value decreased at 55% loading, suggesting that full loading of BPEI into the pores inhibits mass transfer. SC-BPEI adsorbents exhibit two-step weight loss at 180 - 210 °C and over ~ 240 °C. Interestingly, the decomposition peak temperature $T_p$ increased with decreasing BPEI loadings (Figure 4B), due to the formation of amine-silanol ion pairs. Outer layers interaction decreases as the amine layers became thicker. Continuous weight loss at above 200 °C indicated multilayer BPEI coating with different thermal stabilities.

To summarize, extracted platelet silica SE could retain higher porosity than calcined platelet silica SC during amine functionalization. Surface silanols interact with BPEI amine chains, thus increasing the thermal stability of the adsorbent.

3.3 Silanol-amine cooperative CO$_2$ adsorption on amine-grafted platelet silicas

BPEI grafting is a two-step process: silane coupling agent Cl-PTES condensed with the silanols, and BPEI substituted the chlorine in Cl-PTES. The detailed grafting mechanism was studied by $^{29}$Si MAS NMR (Figure S2) and X-ray photoelectron spectra (Figure S3).

The CO$_2$ adsorption capacity of SC-G-BPEI dropped as the temperature was increased, due to an exothermic adsorption mechanism (Figure 5). Interestingly, the CO$_2$ adsorption capacity on SE-G-BPEI reached a maximum at 40 °C (1.97 mmol/g). This adsorption behavior is normally observed in adsorbents that are physically
impregnated with over 30% amines, explained by a diffusion barrier in thick amine layers\textsuperscript{9,15}. However, the adsorbents in this study are chemically grafted with amines at an amine loading of only \sim 14\%. At such a low amine loading and layer thickness, the diffusion barrier is relatively low, thus other factors may be at work. Based on the surface chemistry of the adsorbents, we propose the following explanation. Surface silanols form ion pairs with amines\textsuperscript{25} and higher surface silanol density may result in stronger interactions. Such ionic interactions compete with CO\textsubscript{2} adsorption reaction. At elevated temperatures up to 40 °C, silanol-amine interactions might become unstable, allowing more amine groups to react with CO\textsubscript{2}. At 60 °C, the exothermic nature of adsorption began to dominate, causing a decrease in the adsorption capacity. The fact that maximum adsorption at a higher temperature was only observed in the silanol-rich adsorbent also supports the hypothesis.

The FTIR spectra of platelet silica before and after amine modification are shown in Figure 6A. The bands at \sim 3425 cm\textsuperscript{-1} and 1630 cm\textsuperscript{-1} correspond to stretching and bending vibration of physically adsorbed water\textsuperscript{19,26,27}. All samples showed the IR peaks corresponding to symmetric stretching vibration (800 cm\textsuperscript{-1}) and asymmetric stretching vibration (1080 cm\textsuperscript{-1}) of Si–O–Si silica framework, indicating that the samples retained the Si-O-Si framework after modification\textsuperscript{19,28}. A relatively narrow band at 3745 cm\textsuperscript{-1} (Figure 6) indicates the presence of free Si–OH groups on the silica surface\textsuperscript{19,27,29}. The existence of these free silanols should be attributed to two reasons.
The amine grafting density is 1.97 mmol N/g for SC-G-BPEI, and 3.35 mmol/g for SE-G-BPEI, while the silanol group densities are 6.27 mmol -OH/g for SC and 11.0 mmol -OH/ g for SE. This means that the amine grafting density is only about 30 % of the surface -OH group density on the silica supports, suggesting that a considerable amount of silanols remained free -OH groups. Another possible source of free silanols is the hydrolysis of the silane coupling agent Cl-PTES, giving rise to 3 silanols per molecule and not all of them are used for grafting. In other words, only a part of the silanol groups were attached to the amines through covalent or hydrogen bonds, while the others remained as free silanols.

In amine-grafted samples, an additional wide absorbance of -NH- and -NH₂ could be seen at 3000-3200 cm⁻¹, overlapping with the OH band¹⁶, suggesting the successful loading of amine groups after grafting. The attachment of organic groups was confirmed by the appearance of asymmetric and symmetric CH₂ stretches at 2960 and 2848 cm⁻¹. It can thus be concluded that BPEI were anchored onto the surface⁶. Bands at ~1560 cm⁻¹ and ~1470 cm⁻¹ corresponded to COO⁻ asymmetric stretching and NH₃⁺ symmetric deformation, typically observed on carbamates ion pairs²⁷, ³⁰. Carbamate is probably formed by pre-adsorbed CO₂ in the air and the highly reactive amine groups. Additionally, these bands could explain the pre-adsorbed CO₂ species in the TGA curves (Figure 4).
It is well known that amine based adsorbents reacts with CO$_2$ on a 2:1 ratio under dry conditions. Interestingly, the amine efficiency of both adsorbents exceeded the theoretical 0.50 mmol CO$_2$/ mmol N under dry condition (Figure 5). To explain the reaction mechanism underlying the high amine efficiency, we compared the ATR-IR fingerprint spectra of the two adsorbents after CO$_2$ saturated adsorption (Figure 6B). To prevent the effect of adsorbed water and CO$_2$, we have sealed the ATR chamber throughout the IR measurement.

The possible products formed during CO$_2$ adsorption are ammonium carbamate$^{27}$ ($\text{NH}_3^+\text{COO}^-$, 1650, 1563, 1473 and 1390 cm$^{-1}$), carbamic acid dimers$^{27, 29}$ ($\text{R}^1\text{N(COOH)}_2\text{R}^1\text{N}$, 1696 cm$^{-1}$), silylpropyl carbamate$^{26, 28}$ ($\text{R}^1\text{NCOO-Si}$, 1514 cm$^{-1}$), bicarbonate$^{26, 27}$ (HO-COO$, 1423 \text{ cm}^{-1}$). Interestingly, the bands of ammonium carbamate in SE-G-BPEI shifted to higher wavenumbers, indicating stronger hydrogen bonding near the silica surface. This is in good agreement with the higher silanol density in SE leading to more silanol amine interactions.

Based on these IR species and mechanistic knowledge to date$^{19, 26-30}$, we propose 4 possible reaction pathways for CO$_2$ adsorption on BPEI-grafted platelet silica, as shown in the following equations and in Scheme 2:

1. Two primary or secondary amine groups react with one CO$_2$ to form an ammonium carbamate:

$$\text{CO}_2 + \text{R}^1\text{NH} + \text{R}^2\text{NH} \leftrightarrow \text{R}^1\text{NH}_2^+ + \text{R}^2\text{NCOO}^- \quad (I)$$
Where R\textsuperscript{1} and R\textsuperscript{2} are different BPEI chains.

(2) One primary or secondary amine group and one silanol react with one CO\textsubscript{2} to form silylcarbamate:

\[
\text{CO}_2 + R^1\text{NH} + \text{Si-OH} \leftrightarrow \text{Si-OH}^+ + R^1\text{NCOO}^- \leftrightarrow R^1\text{NCOO-Si} + \text{H}_2\text{O} \quad \text{(II)}
\]

Oxonium \hspace{1cm} Silylcarbamate

Here surface silanol (Brønsted base) accepts a proton from R\textsuperscript{1}NH (Brønsted acid).

(3) One water molecule formed in reaction (II) and a tertiary amine group react with one CO\textsubscript{2} to form bicarbonate:

\[
R_3\text{N} + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow R_3\text{NH}^+ + \text{HO-COO}^- \quad \text{(III)}
\]

Ammonium \hspace{1cm} Bicarbonate

(4) Primary or secondary amines react with CO\textsubscript{2} with a 2:2 stoichiometry to form carbamic acid dimer.

\[
2\text{CO}_2 + 2R^1\text{NH} \leftrightarrow 2R^2\text{NCOO}^+ \leftrightarrow R^1\text{N} (\text{COOH})_2R^1 \quad \text{(IV)}
\]

Carbamic acid \hspace{1cm} Carbamic acid dimer

Under dry conditions, CO\textsubscript{2} adsorption follows the stoichiometry of amine: CO\textsubscript{2} = 2:1. Mechanism (II), (III) and (IV) have a stoichiometry of amine: CO\textsubscript{2} = 1: 1, which improves the amine efficiency. After grafting, the remaining silanols could be utilized in adsorption through mechanism (II) and (III). This explains why the amine utilization efficiency of the two adsorbents were more than 0.50 mmol CO\textsubscript{2}/ mmol N.
under dry condition. In other words, the cooperative effect of silanol and amine groups improves the CO$_2$ adsorption efficiency of the adsorbents.

### 3.4 CO$_2$ adsorption behavior of amine-impregnated platelet silica adsorbents

To evaluate important parameters in CO$_2$ adsorption (i.e. pore size, pore length, amine molecular weight, amine loading, temperature and silanol density), a series of adsorption tests were carried out in a lab-assembled fixed-bed reactor system. The effects of pore structure and amine molecular weight on CO$_2$ adsorption were compared in Figure S4 and Figure S5. At low amine molecular weight ($M_w=600$), pore length $L$ affects CO$_2$ adsorption, as both SC-BPEI-50 ($L=300$ nm) and SCF-BPEI-50 ($L=300$ nm) outperform SBA-15-BPEI-50 ($L=1000$ nm) by over 70% in CO$_2$ adsorption. With increasing $M_w$ from 600 to 1800, the pore size $D_p$ started to play a role. CO$_2$ adsorption decreased by ~40% over SCF-BPEI-50 ($D_p = 10.8$ nm), and only ~10% over SC-I-BPEI-50 ($D_p = 13.8$ nm). The lower decrease indicated better amine distribution and CO$_2$ diffusion inside larger pores. Further increasing $M_w$ to 10000 resulted in sharp decrease of CO$_2$ adsorption in all three adsorbents due to pore clogging by long chain amines.

Results in Figure 7 indicate that silanol densities affected CO$_2$ adsorption behaviors. At 10 and 20% BPEI loading, the CO$_2$ adsorption capacity over BPEI-silica adsorbents dropped with increasing temperature, due to thermodynamic limitations. In contrast, over 30 wt.% BPEI loading, CO$_2$ adsorption capacity
increased with elevated adsorption temperature. Moreover, the maximum CO$_2$ adsorption shifted to higher temperatures with increasing amine loading. These phenomena indicated diffusion controlled adsorption. At 30% loading, both SE-I-BPEI-30 and SC-I-BPEI-30 retained similar adsorption capacity in the whole temperature range. A clear difference was seen at 50% BPEI loading. SE-I-BPEI-50 reached maximum CO$_2$ adsorption at 75 °C, while CO$_2$ adsorption on SC-I-BPEI-50 continued to increase. As reported by Heydari-Gorji et al., such adsorption behavior indicates better CO$_2$ diffusion in SE-I-BPEI, probably related to the higher porosity in SE-I-BPEI-50 (Table 2). At 55% BPEI loading, both adsorbents exhibit typical diffusion limited adsorption behavior, because all porosity is lost at this loading.

Higher silanol density led to better amine dispersion and higher porosity (Table 2, Scheme 1), thus improved adsorption capacity and efficiency. At 65 °C, the adsorption efficiency of SE-I-BPEI-30 reached 565.7 mg-CO$_2$ / g-PEI, which is the highest value ever reported in amine-impregnated silica adsorbents. At 75 °C, SE-I-BPEI-50 absorbed 5.65 mmol CO$_2$/g, or 526.7 mg-CO$_2$ / g-PEI, which are the highest adsorption capacity and amine efficiency ever reported in CO$_2$ adsorbents at this amine loading (Table 3).

Amines with a longer chain have a long service life due to less evaporation over prolonged adsorption-desorption cycles. The most promising adsorbents, SE-I-BPEI-50 and SC-I-BPEI-50, underwent 20 CO$_2$ adsorption-desorption cycles. The
CO$_2$ adsorption capacities and breakthrough behavior remained essentially unchanged after 20 adsorption-desorption cycles (Figure 8 inset), suggesting minor amine degradation and stable kinetics. Complete CO$_2$ desorption was achieved over 20 cycles, due to a better stability of BPEI-1800. Relatively mild regeneration conditions are needed, possibly due to lower heat of desorption of CO$_2$-tertiary amine. Mild regeneration not only saves energy and equipment costs, but also prevents amine evaporation or degradation.

3.5 Kinetic and diffusion modeling of CO$_2$ adsorption

To better understand the adsorption kinetics, different models$^{31, 32}$ (see supplementary information for detailed model theories) were used to fit the experimental data.

Adsorption data deviated from pseudo-second or pseudo-first models, but fitted well with the Avrami model$^{31}$ (Figure 9), suggesting that CO$_2$ adsorption was not simple physical nor chemical mechanism, but a combination of both. In Avrami model, the kinetic parameters $k_n$ and $n$ are affected by reaction temperature and BPEI loading (Table 4). The fractional order $n$ ranged between 1.38-1.60 (Table 4), indicating the coexistence of chemical and physical mechanisms.

$n$ decreased with increasing temperature, indicating that chemical adsorption is suppressed. This is consistent with the adsorption behaviors shown in Figure 7. The
overall CO₂ adsorption rate kₐ also decreased with increasing amine loading, due to the increase of pore diffusion resistance.

The Avrami model illustrated temperature and loading effects on CO₂ adsorption, but it provides no information regarding CO₂ diffusion. Therefore, the kinetic data were fitted to two diffusion models to further understand how diffusion process affects CO₂ adsorption.

The Boyd’s film diffusion plots for two adsorbents at different temperatures are non-linear (Figure 10), suggesting that film diffusion is the rate-determining step in adsorption. Moreover, the slope of the curves decreased with increasing adsorption temperature, and the fitted intercept approached the origin. This tendency suggested that higher temperature reduced film thickness and pore diffusion started to play a role.

Fitting to the intraparticle diffusion model showed three near-linear regions related to three adsorption steps during the adsorption process (Figure 11). The three steps correspond to film diffusion, pore diffusion and attributed to saturated adsorption. Before the equilibrium stage III, the slope of the fitting curve indicates the diffusion rate. Film diffusion (stage I) is slower and thus the overall rate-controlling step, in agreement to Boyd’s model (Figure 10). The slope of step II represented the pore diffusion rate. Interestingly, the value of slope II follows: SBA-15-I-BPEI-50 < SC-I-BPEI-50 < SE-I-BPEI-50, which indicates that: 1) short and large mesopores facilitate
pore diffusion; 2) a better-preserved porosity in SE-I-BPEI-50 further improves pore diffusion. This result is also in good agreement with the different adsorption behaviors in Figure 7.

4. Conclusions

CO$_2$ capture by amine-modified mesoporous silica is a promising substitute for the energy-intensive amine scrubbing. Tailoring the adsorbent properties and surface chemistry are important routes to enhance adsorption efficiency. This study focused on understanding the effect of a silanol-rich surface on adsorbent property and CO$_2$ capture performances. Silanols could not only serve as reactive sites for amine grafting, but also as a potential adsorption site, as indicated by infrared spectroscopy. Silanol-rich adsorbents has more favorable amine dispersion and porosity, thereby showing enhanced CO$_2$ pore diffusion. These potential benefits of silanols, coupled with a platelet mesoporous structure and branched polyamine chains, have yielded adsorbents with unprecedented CO$_2$ adsorption capacity (5.65 mmol/ g) and efficiency (526 mg CO$_2}$/ g-PEI).

This study provides further insight into the optimization of amine-silica CO$_2$ adsorbent: (1) Short and large mesoporous structure which favors amine immobilization and CO$_2$ diffusion into the pores. (2) High surface silanol density, which may help enhance CO$_2$ adsorption efficiency and retain more porosity. (3) Branched polyamine with medium molecular weight, such as the BPEI (Mw = 1800)
used in this study. Branched structure has lower viscosity and thus reduced diffusion barrier. Medium molecular weight strikes a balance between amine distribution and stability.

Acknowledgments

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References


Figure legends

Scheme 1 a) BPEI functionalization of calcined platelet silica; b) BPEI functionalization of extracted platelet silica. Red dots and blue curves represents CO$_2$ molecule and BPEI amine chains, respectively.

Scheme 2 Four possible reactions of CO$_2$ on BPEI grafted platelet silicas. Adsorption products are in bold font and red color.
Figure 1 (a) TEM images of platelet silica particles on different scales and orientations, showing the pore length $L = $ and particle radius $R$. (b) $N_2$ adsorption-desorption isotherms at 77 K and KJS pore size distribution (inset) of calcined (SC) and extracted platelet silica (SE). Isotherm of SE was shifted up by 300 cm$^3$/g for clarity.

Figure 2 TGA curves of calcined platelet silica (SC) and extracted platelet silica (SE) under a nitrogen flow at heating rate of 10 °C/ min.

Figure 3 Nitrogen adsorption-desorption isotherms of BPEI grafted (hollow) and BPEI impregnated (solid) platelet silica sorbents. The isotherms are shifted up with a 100 cm$^3$/g offset for clarity.

Figure 4 (A) thermogravimetric analysis (TGA) curves and (B) differential thermogravimetric curves of SC and BPEI-impregnated adsorbents. Weight loss before 100 °C corresponded to pre-adsorbed moisture and CO$_2$.

Figure 5 CO$_2$ adsorption capacities and efficiencies of BPEI grafted platelet silica sorbents.

Figure 6 (A) FT-IR spectra of (a) SC; (b) SC-G-BPEI; (c) SE; (d) SE-G-BPEI. The absorbance was offset by 0.35 for clarity; (B) IR fingerprint difference spectra after 30 min saturated adsorption of CO$_2$ (10 %, 30 mL/min) at 30 °C: a) SE-G-BPEI-CO$_2$;
b) SC-G-BPEI-CO$_2$. Atoms and bonds corresponding to the IR signal are in bold and red font. The samples were obtained immediately after CO$_2$ adsorption and sealed in a tube saturated with dry CO$_2$ atmosphere. To prevent the effect of adsorbed water and CO$_2$, the ATR chamber was sealed throughout the IR measurement.

Figure 7 CO$_2$ adsorption capacities of BPEI-impregnated adsorbents at different temperatures and amine loadings in a simulated flue gas (10 % CO$_2$ and 90 % N$_2$).

Figure 8 CO$_2$ adsorption breakthrough curves at first and last adsorption cycle and adsorption capacity of regenerated adsorbents in each adsorption-desorption cycle (inset). Adsorption conditions: 75 °C, 30 mL/ min, 10 % CO$_2$ in N$_2$; desorption conditions: 90 °C, pure N$_2$ purge, 60 mL/ min.

Figure 9 kinetic fitting of CO$_2$ adsorption on SE-I-BPEI-50 at different temperatures. (a) pseudo-first model; (b) pseudo-second order model; (c) Avrami model.

Figure 10 Fit to Boyd film diffusion model of BPEI impregnated adsorbents at different CO$_2$ adsorption temperature. A linear fit means that film diffusion does not plays a role in adsorption.

Figure 11 Fit to pore diffusion model of CO$_2$ adsorption at 75 °C on different BPEI-impregnated adsorbents: a) SBA-15-BPEI-50; b) SC-I-BPEI-50; c) SE-I-BPEI-50.
Figure S1 Effects of TEOS and decane amount on the morphology of silica particles.

(P123/NH₄F/TEOS/decane were (a) 1: 20: 235; (b) 1: 40: 235; (c) 1: 60: 235; and (d) 1: 77: 235; (e) 1: 60: 134; (f) 1: 60: 235; (h) 1: 60: 755.

Figure S2 Chemical shifts of SC a) before and b) after grafting Cl-PTES. Q2, Q3, and Q4 correspond to silicon tetrahedrons with 2, 3 and 4 Si-O-Si bonds, respectively. Self-condensation forms two types of oligomers, referred to as S1 and S2.

Figure S3. C 1s X-ray photoelectron spectra (a) before grafting BPEI (b) after grafting BPEI.

Figure S4 N₂ adsorption isotherms and pore size distribution (inset) of three different silica supports. The isotherms are offset by 300 cm³/g for clarity.

Figure S5 CO₂ adsorption capacity at 75 °C over three silica supports impregnated with 50 % BPEI.

**Table legends**

Table 1 Dosages of BPEI and platelet silica for amine impregnation

Table 2 Pore parameters of different silica supports and BPEI-silica adsorbents

Table 3 literature survey of CO₂ adsorption capacities and amine efficiency of PEI impregnated silica adsorbents

Table 4. Kinetic fitting results from Avrami model
Table S1 IR peak assignment of functional groups

Table S2 IR fingerprint assignment of specific adsorbed specie
<table>
<thead>
<tr>
<th>Total mass/ g</th>
<th>BPEI/ g</th>
<th>Platelet silica/ g</th>
<th>Amine loading/ %</th>
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<tr>
<td>1.0</td>
<td>0.10</td>
<td>0.90</td>
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<tr>
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<td>55</td>
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Table 2 Pore parameters of different silica supports and BPEI-silica adsorbents

<table>
<thead>
<tr>
<th>Material</th>
<th>( W_{\text{BPEI}} )(^a) (%)</th>
<th>( S_{\text{BET}} )(^b) (m(^2)/g)</th>
<th>( V_{\text{P}} )(^c) (cm(^3)/g)</th>
<th>( D_{\text{P}} )(^d) (nm)</th>
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<td>SC(^e)</td>
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<tr>
<td>SE(^f)</td>
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<td>1.31</td>
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<td>SCF(^g)</td>
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<tr>
<td>SC-Cl-PTES(^h)</td>
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<td>SE-Cl-PTES</td>
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<td>SC-G-BPEI(^i)</td>
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<td>29.2</td>
<td>0.115</td>
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</table>

a) \( W_{\text{BPEI}} \) – BPEI loading (weight percentage) measured by elemental analysis;
b) \( S_{\text{BET}} \) – BET surface area;
c) \( V_{\text{P}} \) – pore volume calculated at relative pressure \( P/ P_0 = 0.995 \);
d) \( D_{\text{P}} \) – most probable pore size from the adsorption branch using KJS method;
e) SC – calcined platelet silica;
f) SE – extracted platelet silica
g) SCF – platelet silica synthesized only adding NH₄F but without decane.

h) Platelet silica grafted with silane coupling agent Cl-PTES.

i) Platelet silica further grafted with BPEI.

Table 3 literature survey of CO₂ adsorption capacities and amine efficiency of PEI impregnated silica adsorbents

<table>
<thead>
<tr>
<th>Support type</th>
<th>PEI type ^a-M_w^- loading (%)</th>
<th>q_e(CO₂)^b</th>
<th>Ads. Effic^ce</th>
<th>P_CO₂^d</th>
<th>Te</th>
<th>ref</th>
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<tr>
<td></td>
<td></td>
<td>mmol/g-sorbent</td>
<td>mg/g-PEI</td>
<td>bar</td>
<td>°C</td>
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<tr>
<td>KIT-6</td>
<td>L^a^-800-50</td>
<td>3.00</td>
<td>264.0</td>
<td>1</td>
<td>105</td>
<td>8</td>
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<tr>
<td>KIT-6</td>
<td>L-600-50</td>
<td>3.07</td>
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<td>75</td>
<td>8</td>
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<tr>
<td>Nanosilica</td>
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<td>3.89</td>
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<td>336.7</td>
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<td>10</td>
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<td>SC</td>
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a) Linear (L) or branched (B); b) adsorption capacity; c) adsorption efficiency; d) CO₂ partial pressure; e) adsorption temperature; f) samples prepared in this work.
Table 4. Kinetic fitting results from Avrami model

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<th>T</th>
<th>k\textsubscript{n}</th>
<th>q\textsubscript{e} (exp)</th>
<th>q\textsubscript{e} (fit)</th>
<th>n</th>
<th>R\textsuperscript{2}</th>
<th>Err</th>
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<td>mmol/g</td>
<td>mmol/g</td>
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<td>SBA-15-I-BPEI-50</td>
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<td>1.42</td>
<td>0.991</td>
<td>0.237</td>
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<tr>
<td></td>
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<td>4.66</td>
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<td>4.88</td>
<td>1.38</td>
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</table>

a) k\textsubscript{n} is the mass transfer constant;

b) Adsorption capacity [mmol/g] determined by fixed bed adsorption experiments;

c) Adsorption capacity [mmol/g] calculated from kinetic models;

d) n is the kinetic order of the Avrami model, also the Pseudo order of reaction. n closer to 2 indicates a second order (chemical) reaction, while n closer to 1 represents a first order (physical) reaction mechanism;
e) Regression coefficient which determines how well the data points fit any model. $R^2$ value is higher for Avrami model, indicating a better fit of the experimental data than the other two models;

f) Standard Error of the adsorption capacity.
Table S3 IR peak assignment of functional groups

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<tr>
<th>Wavenumber</th>
<th>assignment</th>
<th>corresponding group</th>
<th>ref</th>
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<td>3700</td>
<td>O-H symmetrical stretching</td>
<td>silanols</td>
<td>2</td>
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<tr>
<td></td>
<td>vibration</td>
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<td></td>
</tr>
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<td>3425</td>
<td>O-H stretching vibration</td>
<td>silanols, physisorbed water</td>
<td>4, 5</td>
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<td>2960</td>
<td>C-H asymmetric stretch</td>
<td>alkyl chain</td>
<td>6, 7</td>
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<td>2848</td>
<td>C-H symmetric stretch</td>
<td>alkyl chain</td>
<td>6, 7</td>
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<td>7</td>
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<td>N-H bending vibration</td>
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<tr>
<td>~ 960</td>
<td>Si–O in-plane stretching</td>
<td>silica framework</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>vibrations</td>
<td></td>
<td></td>
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<tr>
<td>~ 800</td>
<td>Si-O symmetric stretching</td>
<td>silica framework</td>
<td>5</td>
</tr>
<tr>
<td>~ 615</td>
<td>C–H vibration</td>
<td>silica framework</td>
<td>5</td>
</tr>
<tr>
<td>~ 460</td>
<td>Si-O bending vibration</td>
<td>silica framework</td>
<td>5</td>
</tr>
</tbody>
</table>
Table S4 IR fingerprint assignment of specific adsorbed species

<table>
<thead>
<tr>
<th>Wavenumber</th>
<th>Assignment</th>
<th>corresponding group</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>~ 1715</td>
<td>C=O stretching</td>
<td>Silylpropyl carbamate</td>
<td>8, 9</td>
</tr>
<tr>
<td>~ 1696</td>
<td>C=O stretching</td>
<td>Carbamic acid dimer</td>
<td>8, 10</td>
</tr>
<tr>
<td>~ 1650</td>
<td>NH(^+) asymmetric deformation</td>
<td>ammonium ion</td>
<td>4, 7</td>
</tr>
<tr>
<td>~ 1563</td>
<td>COO(^-) asymmetric stretching</td>
<td>carbamate</td>
<td>4, 10</td>
</tr>
<tr>
<td>~ 1514</td>
<td>NH deformation, C-N silylpropyl carbamate</td>
<td>9, 10</td>
<td></td>
</tr>
<tr>
<td>~ 1473</td>
<td>NH(_3^+) symmetric deformation</td>
<td>carbamate</td>
<td>8, 9</td>
</tr>
<tr>
<td>~ 1423</td>
<td>COO symmetric stretching</td>
<td>bicarbonate</td>
<td>9</td>
</tr>
<tr>
<td>~ 1390</td>
<td>NCOO skeletal vibration</td>
<td>carbamate</td>
<td>7, 10</td>
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</tbody>
</table>
Figure a shows a close-up view of the material, indicating the presence of macropores. The sizes are labeled with 'R' and 'L', with scales provided at 200 nm and 1 μm.

Figure b presents a graph showing the quantity adsorbed (cm$^3$/g, STP) versus relative pressure (P/Po) for two samples, denoted as SC and SE. The inset graph displays the pore width (nm) against the derivative of the adsorption-desorption isotherm.
a) $q_i = 1.21 t^{0.5} - 1.28$
$R^2 = 0.990$

b) $q_i = 1.56 t^{0.3} - 2.14$
$R^2 = 0.990$

c) $q_i = 1.65 t^{0.2} - 2.42$
$R^2 = 0.995$
6.65 Si–OH/nm²

OH

OH

OH

OH

OH

OH

11.0 Si–OH/nm²

OH

OH

OH

OH

OH

OH

OH

OH

OH

OH

a ➔ Impregnation ➔ b

6.65 Si–OH/nm²

OH

OH

OH

OH

OH

OH

OH

OH

11.0 Si–OH/nm²

OH

OH

OH

OH

OH

OH

OH

OH

OH

OH

OH
**Highlights:**

- Solvent extraction creates a silanol-rich surface on platelet silica.
- Silanol-amine cooperation enhanced CO$_2$ adsorption efficiency.
- Silanol-rich surface improved amine loading and distribution inside the pores.
- Silanol-rich amine-silicas showed highly efficient and reversible CO$_2$ adsorption.